

# Kondo resonance line-shape of magnetic adatoms on decoupling layers

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The zero-bias resonance in the  $dI/dV$  tunneling spectrum recorded using a scanning tunneling microscope above a spin-1/2 magnetic adatom (such as Ti) adsorbed on a decoupling layer on metal surface can be accurately fitted using the universal spectral function of the Kondo impurity model both at zero field and at finite external magnetic field. Excellent agreement is found both for the asymptotic low-energy part and for the high-energy logarithmic tails of the Kondo resonance. For finite magnetic field, the nonlinear fitting procedure consists in repeatedly solving the impurity model for different Zeeman energies in order to obtain accurate spectral functions which are compared with the experimental  $dI/dV$  curves. The experimental results at zero field are sufficiently restraining to enable an unprecedented reliability in the determination of the Kondo temperature, while at finite fields the results are more ambiguous and two different interpretations are proposed.

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When an atom with non-zero spin and/or orbital magnetic moment is adsorbed on an ultrathin insulating (“decoupling”) layer grown on a metal substrate, it will behave as a nearly ideal magnetic impurity with well-defined local moment which is described by the Kondo model [1–4]. The Kondo model explains the effects of the weak coupling of the impurity moment with the itinerant electrons in the substrate. If the coupling is antiferromagnetic, the impurity moment is screened in a complex many-particle process (the Kondo effect [4–7]), the signature of which is a resonance in the impurity spectral function which peaks in close vicinity of the Fermi level [8–11]. The theoretically predicted resonance line-shape is parabolic near its maximum [4, 12], has long tails which can be empirically well fitted by an inverse square root (Doniach-Šunjić) function [13–15], but which have been shown to really be logarithmic [16, 17]; the Kondo resonance cannot be well approximated by a simple Lorentzian resonance [18–20].

Recent tunneling spectroscopy experiments performed at very low temperatures provide  $dI/dV$  spectra of magnetic adatoms with excellent energy resolution and very low noise [21–23]. Numerical techniques for accurately computing impurity spectral functions at finite frequencies have also reached maturity [13, 15, 24–30]. We are thus presently able to directly compare experimental spectra with the theory. This is interesting for several reason. First, it is a non-trivial test of the adequacy of simplified quantum impurity models for describing the low-energy behavior of single magnetic adsorbates. Second, it provides an unbiased approach for extracting the parameters of the impurity model. Third, it confirms our understanding of the logarithmic dynamical behavior of quantum impurities in the intermediate frequency regime (above the Kondo scale, but below the atomic scale). Our goal in this work is to fit the experimental tunneling spectra for a Ti adatom on the  $\text{Cu}_2\text{N}/\text{Cu}(100)$  surface, Fig. 4 in Ref. 23, using Kondo resonance curves calculated using the numerical renormalization group (NRG) technique [20, 31]. The fitting window is the bias voltage window from -10 mV to 10 mV,

which includes not only the Kondo resonance peak but also its long-tailed flanks.

The experimental Kondo-resonance spectrum for Ti shows a sizeable asymmetry between positive and negative bias voltages and the resonance peak is slightly displaced from zero bias. These two features indicate possible presence of additional potential scattering in the problem (in addition to the exchange scattering, which is the crucial element of the Kondo model). It is, however, also possible to account for the asymmetry using a model which takes into account quantum interference between a narrow and a broad scattering channel (similar to the Fano formula used for fitting the spectra of magnetic impurities adsorbed directly on a metal surface [10, 18, 32], but based on the correct impurity spectral function rather than on an approximation by a Lorentzian peak [18, 20]), while the displacement of the peak might be explained by some small bias offset  $V_0$  for experimental reasons (such as thermovoltages generated by temperature differences in the STM head or in the cryostat wiring). As we show in the following, it is indeed possible to obtain an excellent fit to the experimental data with the universal Kondo-resonance line-shape of the symmetric Kondo impurity model; it is not necessary to include any potential scattering in the impurity model itself.

The fitting is performed with the phenomenological ansatz function

$$(dI/dV)(V) = a + b \left[ (1 - q^2) \text{Im} G(eV) + 2q \text{Re} G(eV) \right], \quad (1)$$

where the impurity Green’s function is chosen to be

$$G(\omega) = G_{\text{Kondo}}[(\omega - \omega_0)/\Delta_{\text{HWHM}}]. \quad (2)$$

The ansatz function (1) is chosen so as to reproduce the Fano formula for the case of a pure potential scatterer. The bias voltage is expressed in energy units as  $\omega = eV$ , where  $e$  is the elementary charge;  $\omega_0 = eV_0$  with the voltage offset  $V_0$ . Parameter  $a$  accounts for the possible featureless background conduction, parameters  $b$  and  $\Delta_{\text{HWHM}}$  set the height and width of the resonance, respectively, and  $q$  is a

Fano-model-like asymmetry parameter such that  $q = 0$  describes a symmetric peak, while  $q \neq 0$  leads to an asymmetry. Finally,  $G_{\text{Kondo}}$  is the universal impurity Green's function for the Kondo model, as computed using a highly accurate NRG calculation. It is normalized and rescaled so that in zero magnetic field  $A(\omega = 0) = (-1/\pi)\text{Im } G_{\text{Kondo}}(\omega = 0) = 1$  and  $A(\omega = 1) = 1/2$ . We show in the following that the five-parameter ansatz in Eq. (1) is sufficient to obtain nearly perfect agreement between the experimental results and the theoretical spectral function at zero magnetic field throughout an extended energy range including the resonance peak and its tails. We perform nonlinear fitting using the Levenberg-Marquardt method to obtain the parameter set  $(a, b, \Delta_{\text{HWHM}}, q, \omega_0)$ . To quantify the “goodness of fit” we calculate squared residuals  $\sigma^2$  for all data points.

We first discuss the Kondo resonance in the absence of the external magnetic field,  $B = 0$ . The comparison of the theoretical function, Eq. (1), with the experimental data is shown in Fig. 1 and the extracted parameters are tabulated in Table I (first line). Some comments are in order. First, the asymmetry parameter  $q$  is non-zero, but small. It is not necessary to add some polynomial background to the model in order to describe the asymmetry. A linear background hardly affects the goodness of fit  $\sigma^2$ . A quadratic background somewhat improves agreement in the tails, yet – importantly – the value of  $q$  as extracted using such an extended fit function changes by only 3%. Thus we conclude that the Fano interference is the correct physical interpretation of the observed asymmetry. To further support this claim, additional calculations have been performed for the Kondo model with potential scattering, the Kondo model with conduction-band density of states with a finite slope, as well as for the asymmetric single-impurity Anderson model; the results indicate that it is not possible to reproduce the observed asymmetry without including the Fano-like interference in the ansatz function, except for rather extreme (and thus unphysical) values of the parameters in those models.

The second comment concerns the parameter  $\Delta_{\text{HWHM}}$ . Accurate NRG calculations indicate that the relation between the HWHM of the spectral function for spin-1/2 Kondo model at the particle-hole symmetric point and the Kondo temperature (as defined by Wilson) is [30]

$$\Delta_{\text{HWHM}}/T_{K,W} \approx 3.7. \quad (3)$$

We thus find  $k_B T_{K,W} = 0.176 \text{ meV}$  or

$$T_{K,W} = 2.04 \text{ K}. \quad (4)$$

Away from the particle-hole symmetric point the ratio  $\Delta_{\text{HWHM}}/T_{K,W}$  is different (it depends on the quasi-particle scattering phase shift) [30]. It is also worth mentioning that there are several different definitions of the Kondo temperature for the  $S = 1/2$  Kondo model which are in common use. The Wilson's definition  $T_{K,W}$  is often used in NRG, perturbation theory, and Bethe Ansatz studies, another definition  $T_K^{(0)}$  is used in local Fermi liquid works, and a third definition  $T_{K,H}$  has been used in the works of Hamann, Nagaoka

and Suhl. They are related through  $T_{K,W} = 0.4128 T_K^{(0)}$  and  $T_{K,H} = 2.2 T_{K,W}$ . We thus find

$$\begin{aligned} T_K^{(0)} &= 4.94 \text{ K}, \\ T_{K,H} &= 4.49 \text{ K}. \end{aligned} \quad (5)$$

Some care is needed when comparing works where the Kondo temperature is defined in non-equivalent ways.

The final third comment concerns the thermal broadening. The calculation has been performed at  $T = 0$ , while the experiment [23] is performed at  $T = 500 \text{ mK}$ , which is smaller than  $T_{K,W}$  only by a factor of four. It is known, however, that the main effect of finite temperature in the  $T < T_K$  range is to reduce the height on the resonance peak and only slightly increase the peak width; the logarithmic tails are not affected significantly. This indicates that the finite-temperature effects are small and that the reliability of the extracted parameters is not reduced. The NRG calculation can be performed at finite temperature, but this does not improve the quality of the fit in the present case. Nevertheless, it would be interesting to repeat the experiment at even lower temperature in an attempt to achieve the true asymptotic zero-temperature limit and to reduce the noise even further.

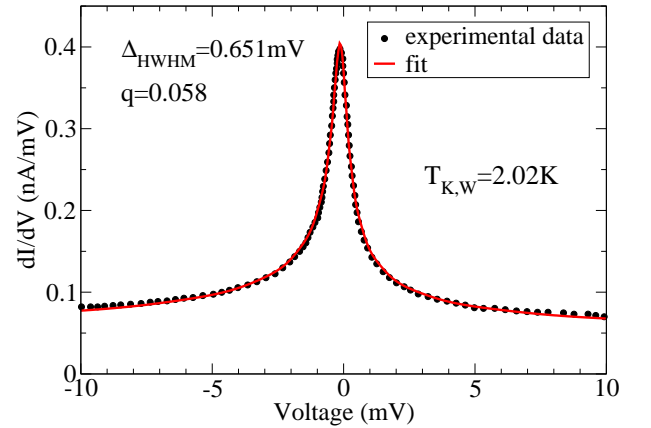


Figure 1: (Color online) Theoretical function (light line, red online) and experimental data (black symbols) for the Kondo resonance in the  $dI/dV$  spectral function for a Ti magnetic impurity atom adsorbed on the  $\text{Cu}_2\text{N}$  layer on  $\text{Cu}(100)$  surface. The theoretical function is given by Eq. (1), the parameters are explained in the main text. The experimental results have been extracted from Fig. 4 in Ref. 23.

For reference, in Fig. 2 we plot a number of spectral line-shapes for Fano-like interference processes for cases where the narrow resonant scattering channel is described either by a Lorentzian curve or by a Kondo resonance curve (see also Refs. 20, 33). The width of the Lorentzian has been fixed so that in the asymptotic low-energy region both curves overlap. As a general rule, at the same value of the asymmetry  $q$  the “Fano-Kondo” line-shapes have longer tails and smoother variation compared to their “Fano-Lorentzian” counterparts. In particular, it should be noted that the experimental  $dI/dV$  curve in Fig. 1 cannot be well described using a Fano-Lorentzian line-shape.

Parameter	$a$	$b$	$q$	$\Delta_{\text{HWHM}}$	$\omega_0$	$g\mu_B B/T_K$
$B = 0$ T	$0.0239 \pm 0.0008$	$-0.00472 \pm 0.00002$	$0.058 \pm 0.003$	$(0.651 \pm 0.008)$ meV	$(-0.116 \pm 0.003)$ meV	0 (*)
$B = 7$ T (A)	$0.3112 \pm 0.001$	$-0.00417 \pm 0.00005$	$0.021 \pm 0.007$	$(0.651 \pm 0.008)$ meV (*)	$(-0.16 \pm 0.01)$ meV	5.14
$B = 7$ T (B)	$0.3112 \pm 0.0005$	$-0.0052 \pm 0.0002$	$0.029 \pm 0.003$	$(0.409 \pm 0.002)$ meV	$(-0.133 \pm 0.003)$ meV	7.36

Table I: Full set of fit parameters for the Kondo resonance peaks shown in Figs. 1 and 3. The error estimates indicated include only the standard deviation from the fitting procedure. The asterisk indicates a parameter whose value is fixed in the minimization.

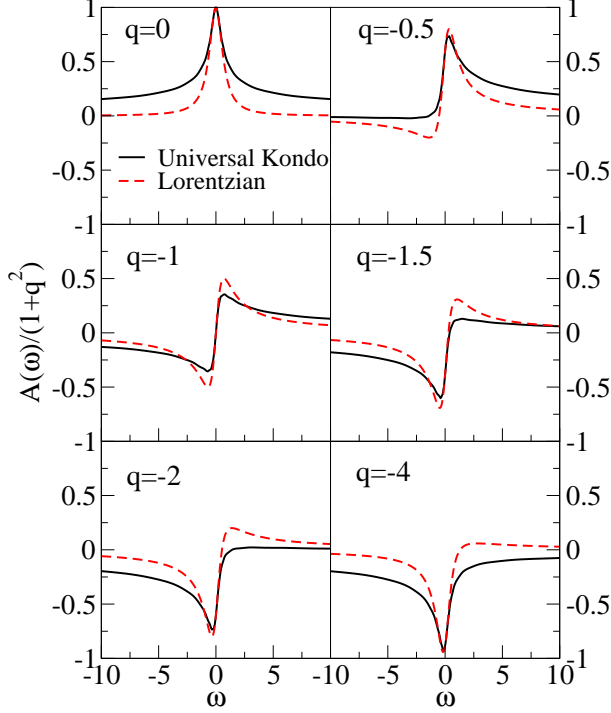


Figure 2: (Color online) Comparison of the resonance line-shapes arising from Fano-like quantum interference in processes where the resonant channel is described by a Lorentzian (dashed line, red online) or by the Kondo resonance curve (full line, black online).

We now turn to the  $dI/dV$  spectra in the presence of the magnetic field, where the splitting of the Kondo resonance is observed [34–38]. We need to establish the value of a new parameter, the Zeeman energy  $b = g\mu_B B$ . We note that while  $B$  is known from the experiment, the  $g$ -factor is not and needs to be determined by the fitting procedure that we now perform. This is a very non-trivial task, since the Kondo resonance splitting is not linear as a function of the Zeeman energy [34–36, 39]. For each value of the ratio  $b/T_K$  a different universal (split) Kondo resonance curve needs to be computed [42]. In minimizing the parameters in the model function, Eq. (1), we first fix  $\Delta_{\text{HWHM}}$ : this choice is equivalent to assuming that the magnetic field does not change the effective exchange coupling  $J_K$  of the impurity spin, which is a reasonable assumption. The resulting fit is shown in Fig. 3 (top panel), the parameters are tabulated in Table I (second line, A), and the variation of the residual error as a function of  $b/T_K$  is plotted

in Fig. 4. The agreement is fairly good, but not outstanding: the amplitude of the two resonance peaks is clearly underestimated. From the known field  $B = 7$  K and the extracted  $b/T_K$  ratio, we determine the value of the  $g$ -factor:

$$g = 2.2. \quad (6)$$

This value is in the same range as the  $g$ -factors for other magnetic adatoms on the same surface [21].

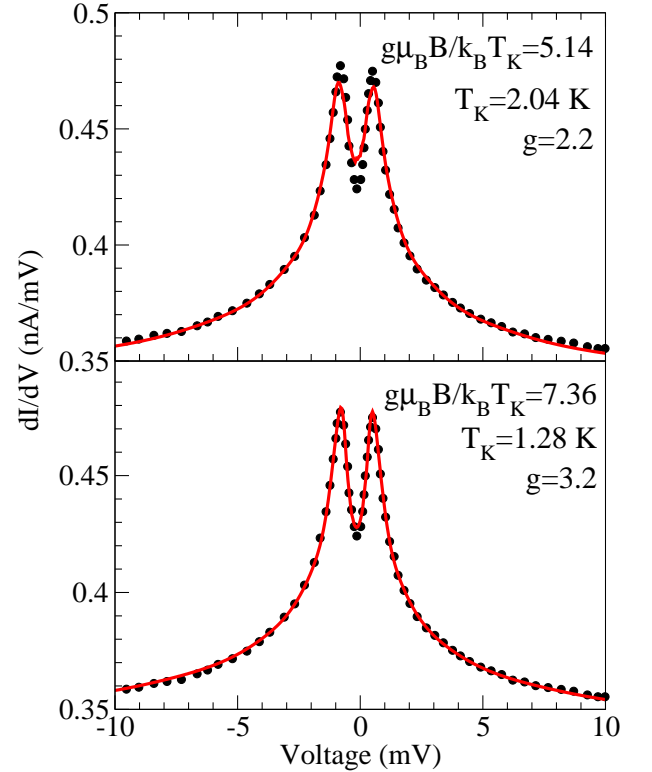


Figure 3: (Color online) Theoretical function (light function, red online) and experimental data (black symbols) for the Kondo resonance splitting in the external magnetic field  $B = 7$  T. Upper panel: fixed parameter  $\Delta_{\text{HWHM}}$ . Lower panel: unconstrained  $\Delta_{\text{HWHM}}$ . The magnetic field strength is 7 B. The experimental data have been extracted from Fig. 4 in Ref. 23.

The fit may be improved by relaxing the constraint that the effective Kondo exchange coupling  $J_K$  does not vary with the magnetic field. The reason for doing so is the observation that the  $S = 1/2$  behavior at low energy scales in Ti adsorbates originates from the freezing out of the  $S = 1$  degree of freedom on some higher energy scales; indeed, a Ti atom in free

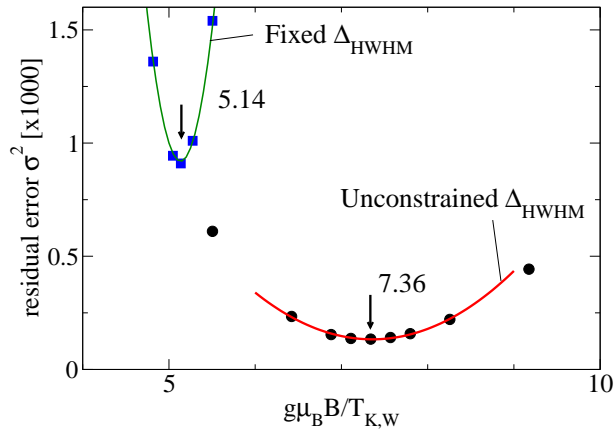


Figure 4: (Color online) “Goodness of fit”  $\sigma^2$  (sum of the residual squared errors) for the field-splitting of the Kondo resonance assuming constant or unconstrained parameter  $\Delta_{\text{HWHM}}$  as a function of the Zeeman energy to Kondo temperature ratio.

space has two  $3d$  electrons and is in a  $S = 1$ ,  $L = 3$  state [23, 40]. Upon adsorption on the surface, the local orbital moment is strongly quenched and the spin moment is also reduced. The presence of the external magnetic field might affect how the original impurity degrees of freedom are combined into an effective  $S = 1/2$  object and how this effective spin is coupled with the substrate electron [41]. Since the Kondo temperature depends exponentially on  $J_K$ , i.e.,  $T_K \propto \exp(-1/\rho J_K)$ , where  $\rho$  is the density of states in the substrate, even a small variation of  $J_K$  might induce a sizable change in  $T_K$ . We thus performed a second fitting calculation where the parameter  $\Delta_{\text{HWHM}}$  was allowed to change. The result of this fit is shown in Fig. 3, bottom panel, and the parameters are listed in Table I, second line (B). The agreement improves significantly, see also the residual errors plotted in Fig. 4. The Kondo temperature determined by this approach is smaller by 40% compared to  $T_K$  at zero field, and the  $g$ -factor is found to be  $g = 3.2$ . While the purported change in  $T_K$  in the field is quite large and the value of  $g$  is larger than typical values for other adatoms, it is not clear whether the improvement of the fit can be solely ascribed to having a further free parameter in the ansatz function (i.e., overfitting) or if there are physical grounds for reduced  $J_K$  in the effective model. This ambiguity calls for further systematic experimental studies.

It has been shown that the zero-bias peaks in  $S = 1/2$  impurities on decoupling layers can be accurately described by the universal Kondo spectral function, confirming the logarithmic frequency-dependence in the resonance tails. The Kondo temperature has been extracted in a reliable way. Due to non-linear behavior of the magnetic-field splitting of the Kondo resonance, two interpretations of the peak structure have been proposed which differ in the values of the exchange coupling  $J_K$  and the  $g$ -factor.

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